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14. ABSTRACT The overall goal of this study is to gain molecular-level understanding of the chemical properties of the diamond-like carbon (DLC) surface exposed at various environmental conditions so that this knowledge can be used to design better DLC coatings and operation conditions. DLC coatings have great potentials to reduce frictional energy loss and increase service life of mechanical systems. However, the near-frictionless and near-wearless behaviors are observed only in vacuum or extremely dry conditions. Our contributions toward the understanding of tribochemical properties of DLC coatings include elucidation of the friction reduction mechanism of hydrogen gas for hydrogen-free DLC coatings, in-situ characterization of the graphite-like transfer film, quantification of the oxidized surface layer and composition on DLC upon exposure to air, the adsorption isotherm of water on DLC in humid air, development of a theoretical model to predict the capillary force at nano-asperity contacts in ambient conditions, and discovery of the vapor phase lubrication method to suppress the wear of DLC in humid air conditions.				
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Project title: Chemical characterization of tribological and biomaterial surfaces with nanoscale spatial resolution

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Accomplishments/New Findings:

1. The friction and wear of hydrogen-free DLC coatings can be reduced by introduction of hydrogen in the tribo-testing environments. A time-of-flight secondary ion mass spectrometry (ToF-SIMS) found that the incorporation of hydrogen to the DLC, resulting from tribochemical reactions of dangling bonds with hydrogen and deuterium was responsible for reduction of friction and improvement of wear resistance.
2. In-situ transmission electron microscopy (TEM) study of diamond-like carbon (DLC) surfaces found evidence that the sp^2 bond content in the tribolayers on highly-hydrogenated near-frictionless carbon (NFC) films is increased upon tribological contacts. The formation of graphite-like layer was not observed for hydrogen-poor DLC surfaces which exhibit high friction and large wear.
3. DLC surfaces are readily oxidized upon exposure to ambient air. The air oxidation alters the chemical composition of the DLC surfaces tested in different environments. Thus, the ex-situ surface analysis of native DLC surfaces tribo-tested in different environments (dry Ar, H_2 , O_2 , humid Ar, and alcohol vapor) cannot provide the chemical information needed for understanding of the environmental effects on DLC friction and wear.
4. The thickness of the oxidized surface layer is about 2~3 nm. The chemical derivatization and x-ray photoelectron spectroscopy (XPS) analysis found that the oxidation products are mostly ether, carbonyl, carboxyl species and a smaller amount of hydroxyl species.
5. The chemical derivatization reaction can differentiate various oxygenated species at DLC surfaces. But, nanoscale chemical imaging of these derivatized species with imaging XPS and scanning Auger electron spectroscopy (AES) was not possible due to poor spatial resolution of XPS and beam damages of the electron beam in AES.
6. The adsorption isotherm of water molecules on DLC under ambient pressure conditions were determined using attenuated total internal reflection infrared (ATR-IR) spectroscopy and ellipsometry. The thickness of the adsorbed water layer is about 1nm at relative humidity between 15% and 80%.
7. A theoretical model was developed to accurately calculate the capillary force at a nano-scale asperity contact due to adsorbed molecular layers. This model will help understand the effect of capillary force on the detrimental effect of humidity on the friction and wear behavior of highly-hydrogenated NFC coatings.
8. The wear of DLC surface rubbing against a stainless steel surface can be suppressed by introducing alcohol vapor into the ambient. The transfer film formation on the stainless steel surface is significantly reduced even though the friction coefficient is not ultra-low in alcohol vapor conditions. This implies that the ultra-low friction coefficient is not necessary condition to attain the wear-free operation of DLC lubrication.
9. For self-mated (DLC-against-DLC) tribo-testing in humid air environments, it was found that the alcohol vapor can completely suppress the wear of DLC surfaces even though the friction coefficient is not ultra-low (higher than 0.1). This implies that the adsorbed alcohol layer can protect the oxidized surface layer on DLC coatings efficiently.

Executive summary

This project advanced understanding of the surface chemical properties of diamond-like carbon (DLC) in ambient air as well as in vacuum. DLC is a scientifically very rich and technologically important coating. Various types of DLC are used to control friction and wear in a wide range of engineering applications nowadays due to their superior mechanical and tribological properties and excellent adhesion to substrates. One of the latest and most exciting developments is hydrogenated DLC coatings which show near-frictionless and near-wearless properties in inert or vacuum environments; thus DLC coatings have great potentials to reduce frictional energy loss and increase service life of mechanical systems. However, such ultra-low friction is observed only in vacuum or extremely dry conditions. In ambient air, the ultra-low friction and wear-free properties are lost. The overall goal of this study is to gain molecular-level understanding of the chemical properties of the DLC surface exposed at various environmental conditions so that this knowledge can be used to design better DLC coatings and operation conditions. Our contributions toward this objective include the in-situ characterization of graphite-like transfer film formed on the counter-sliding surface from the highly-hydrogenated near-frictionless carbon (NFC) films, elucidation of the friction reduction mechanism for hydrogen-free DLC in hydrogen gas environments, quantification of oxidized surface layer and composition on DLC upon exposure to air, the adsorption isotherm of water on DLC in humid air, development of theoretical model to predict the capillary force at nano-asperity contacts in ambient conditions, and discovery of the vapor phase lubrication method to suppress the wear of DLC in humid air conditions.

Brief overview of accomplishments

A. Effect of hydrogen on friction of hydrogen-free DLC

DLC typically combines high hardness and strength with chemical inertness, electrical insulation, optical transparency, and low static and kinetic friction, although these properties may be significantly affected by small changes in the deposition source and environmental conditions [1]. These materials have found extensive use as protective coatings in a number of device applications including automotive gears, magnetic storage disks, biological implants and micro-electromechanical (MEMS) devices [1]. Erdemir et al. have discovered that DLC films with optimum hydrogen contents can reach friction coefficients as low as 0.001 in dry inert environments, and are referred to as “near-frictionless carbon” or simply NFC [2], while hydrogen-free or poorly-hydrogenated DLC films exhibit friction coefficients as high as 1 [3]. It is believed that such a large disparity in their frictional performance may have been associated with a range of intrinsic (film specific) and extrinsic (atmospheric or test condition specific) factors. Intrinsically, the extent of sp^2 vs. sp^3 bonding as well as the amount of hydrogen and/or other alloying elements within the DLC films seem to play significant roles in their mechanical and tribological properties [1]. Externally, the chemical nature (i.e., presence or absence of reactive species) of test environments were found to affect the friction and wear behavior of these films [1,4].

In this project, the tribochemical reactions that reduce the friction of hydrogen-free DLC films in hydrogen gas environments were elucidated with ToF-SIMS analysis. Hydrogen-free or

-poor DLC films performed very poorly in inert or vacuum test environments. Their friction coefficients could be as high as 1. However, when tested under 10 Torr partial pressure of hydrogen or deuterium, their friction coefficients decreased by more than an order of magnitude [5]. A representative example is shown Figure 1a [6]. When tested in 10 Torr Ar, the friction coefficient increased steeply to about 0.7 after sliding for 0.4 m. After reaching 0.65 meter sliding distance, the test was stopped and the background gas was switched to 10 Torr hydrogen. When the sliding experiment was resumed, it was found that the friction coefficient of hydrogen-free DLC was much lower and stabilized at around 0.05. This simple experiment confirmed that hydrogen indeed strongly influences the frictional properties of DLC films [7,8]. Figures 1b and 2c show the total and deuterium ToF-SIMS images of the sliding wear track formed on the DLC-coated disk after test in 10 Torr of deuterium (deuterium was used to distinguish from the background hydrogen peaks in ToF-SIMS). It can be clearly seen that the sliding wear track became very rich in deuterium during the sliding test, suggesting that carbon atoms within the wear track had reacted with deuterium in the surrounding test chamber [6].

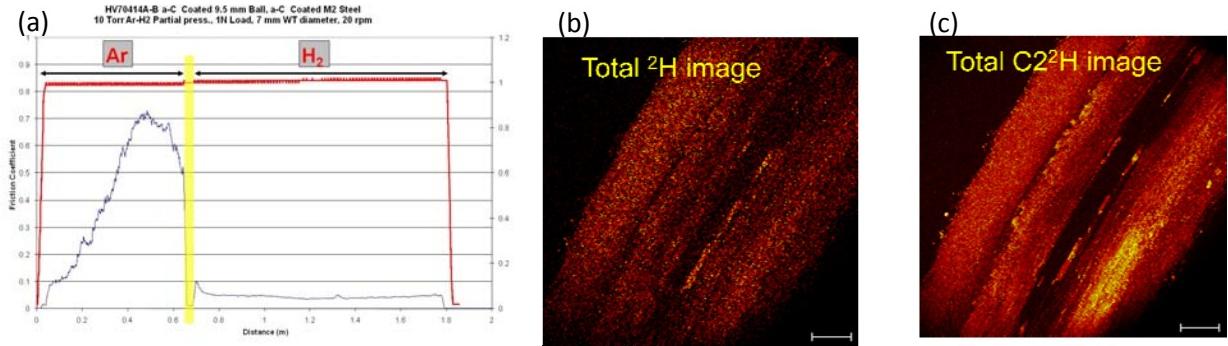


Figure 1. (a) Friction coefficient of hydrogen-free DLC tested in 10 Torr Ar and 10 Torr H₂. (b,c) Total and deuterium ToF-SIMS images of the sliding wear track formed on the DLC-coated disk after test in 10 Torr D₂ [6].

The sudden drop in friction coefficient of hydrogen-free DLC upon introduction of hydrogen into test chamber can be explained as follows. The high and un-steady friction of this test pair in Ar is most likely due to strong dangling bond interactions between carbon atoms on ball and disk side. Deuterium or hydrogen present in the test chamber can react with these surfaces to eliminate most of the dangling bonds and thus eliminate one of the strongest sources of adhesion. Since they are readily available in the surrounding atmosphere, they can continuously replenish and terminate those σ -bonds that may have been created or exposed by mechanical wearing action.

The knowledge gained from these studies may help better understand the fundamental mechanisms that control friction and wear of such films and hence lead to the design of better coatings with much superior tribological properties in practical applications. It will also demonstrate the viability of various lubrication mechanisms proposed for the super-low friction behavior of certain DLC films reported earlier.

B. Tribo-induced bonding modifications in highly-hydrogenated near-frictionless DLC

In-situ tribo-test within a TEM instrument was employed, in collaboration with L. D. Marks at Northwestern University, to characterize the sliding interface between a highly-hydrogenated DLC and a tungsten counter-surface without any postmortem or macroscopic effects that could obscure the interpretation of meaningful results.

It was known that the presence of third bodies or transfer layers is an influential component in determining the friction properties of DLC [9,10]. It has been demonstrated that graphitized transfer layers maintain low and stable friction forces in humid environments [11], mimicking the lubricious behavior of graphite. This previous work conducted friction and wear test *ex situ* and loaded the worn sample and debris into a TEM for examination; thus the surfaces are subject to atmospheric conditions which have significant effects on the surface chemistry (see Sections C and D for details). The in-situ TEM and electron energy loss spectrum (EELS) analyses found that the 1s- π^* transition peak grows as the frictional sliding cycles increases in vacuum [12]. This suggests that a transformation towards a more graphitic material is taking place; possibly an ordered graphitized carbon layer was formed by the mechanical excitation of the film due to the sliding. Neither imaging nor EELS analysis showed any indication of a relative increase in the π^* peak after sliding on the poorly-hydrogenated DLC sample. However, significantly more wear debris was produced, for equal amounts of sliding. This behavior is qualitatively consistent with the macroscopic observation described in Section A. These results suggest that the types of carbon present at the sliding interface govern the friction and wear behavior of DLC and the steady-state near-frictionless behavior of highly-hydrogenated DLC in vacuum is due to wear-induced graphitization [12].

C. Oxidation of DLC upon exposure to air

Not just the type of carbon present at the DLC interface, but also the chemical functional group on DLC surfaces is important especially in ambient air conditions. Hydrogenated DLC films are known to have ultra-low friction coefficients (less than 0.01) in vacuum or inert environments. But, their superlubricity disappears in an ambient environment containing oxygen or water vapor. In contrast, hydrogen-free or poorly-hydrogenated DLC films show a high friction in inert conditions, but their friction coefficient decreases to about 0.1 in humid ambient [1,4].

Figure 2a shows the friction coefficients of a near-frictionless carbon (NFC-6; highly hydrogenated DLC) film sliding against the NFC-6 film [13]. When tested in dry Ar (inert) and dry H₂ (reducing) gases, the initial friction coefficient during the run-in period is about 0.15~0.25 and then gradually decreases to an ultra-low values (<0.02). In dry O₂ (oxidizing) gas, the friction coefficient increases very slowly without showing any run-in behavior. In an Ar environment containing 40% relative humidity (RH), the friction is unstable and varies over a wide range from 0.07 to 0.2. In dry Ar, there is a faint circular mark on the ball surface whose diameter is the same as the Hertzian contact diameter. In dry H₂ and O₂ conditions, some wear debris can be seen although its amount is very small. The humidity in the ambient appears to make the largest difference; there are large deposits on the ball surface which do not look like typical mechanical wear debris. Its appearance resembles some organic liquid deposits.

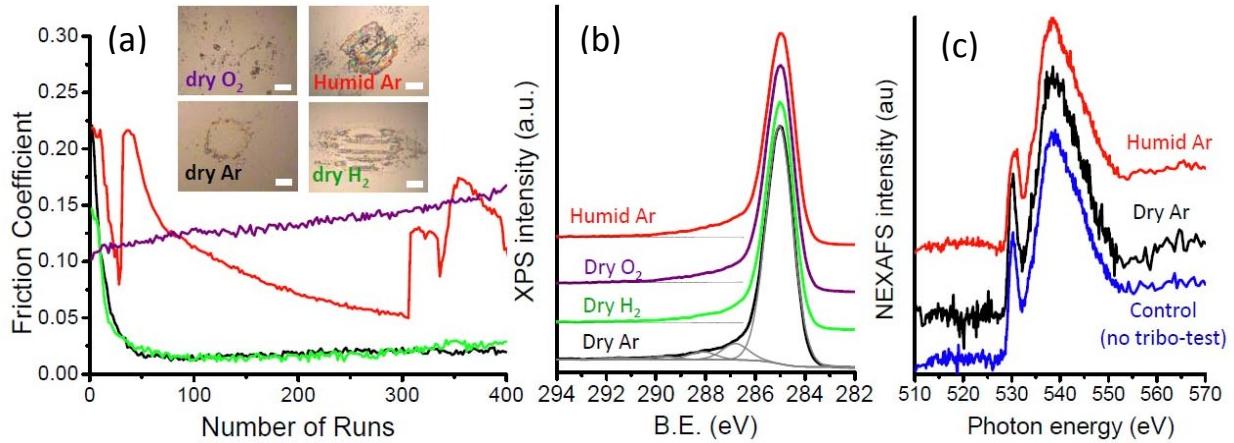


Figure 2. (a) Friction coefficients measured for self-mated highly-hydrogenated DLC (NFC-6) films sliding in dry Ar (black), dry H₂ (green), dry O₂ (purple), and 40% RH Ar (red) environments and optical images of the ball surfaces taken after the friction tests (Hertzian contact pressure $\approx 0.7\text{GPa}$). The scale bar in the image is 20 μm . (b) Ex-situ C1s XPS spectra of NFC-6 tribo-tested in dry Ar, dry H₂, dry O₂, and 40% RH Ar environments. (c) Ex-situ O_K edge NEXAFS spectra of NFC-6 surfaces tribo-tested in dry Ar and 40% RH Ar and comparison with the control sample spectrum [13].

Seeing such drastic differences in friction and wear behaviors of NFC-6, one might expect the surface composition of the tribo-tested region to be significantly different. However, the difference among the ex-situ C1s high-resolution XPS spectra of these samples is negligible (Figure 2b). Similar results can also be found in the literature [14,15]. In the survey analysis, it was found that the oxygen atomic concentration is typically within 9~14%. The spectral difference between the samples does not correlate strongly with the environmental condition in which the tribo-test was made. The data shown in Figure 3b can be fitted to quantify various carbonaceous species: C-C/C-H at 285 eV, C-O at 286.5 eV, C=O at 287.8 eV, and O-C=O at 289.4 eV. Their relative abundances do not show any systematic trends. Also note that the peak at 286.5 eV could be either the hydroxyl (C-OH) or ether (C-O-C) groups, or both, since these groups appear in the same binding energy region.

The tribo-tested samples were analyzed with near-edge x-ray adsorption fine structure (NEXAF) spectroscopy at the Brookhaven synchrotron radiation source. There are two main peaks in the O K-edge NEXAFS spectra (Figure 2c): a sharp peak at 530.1 eV and a broad peak centered at 538.3 eV. These features are consistent with previously reported NEXAFS for DLC [16]. The former can be attributed to the O 1s $\rightarrow \pi^*_{\text{C=O}}$ transition and the latter to O 1s $\rightarrow \sigma^*_{\text{C-O}}$ or $\sigma^*_{\text{C=O}}$. Like the C1s XPS analysis results, there is no clear dependence of the O K-edge spectra on the friction-test environment. They even look the same as the spectrum of the control sample that has not been scratched or tribo-tested at all.

One may argue that the reason for insensitivity of the ex-situ XPS and NEXAF data is due to organic contaminants deposited on the sample. This speculation is easily disputable. First, the XPS and NEXAFS measurements were conducted in UHV conditions, so almost all physisorbed organic contaminants should have already been desorbed during the sample mounting. Second, even a hydroxyl terminated self-assembled monolayer (SAM) on gold show

much less airborne contamination in XPS than DLC coatings. Water contact angle measurements imply that the surface energy of DLC is lower than the OH-terminated SAM; thus, the surface contamination issue is expected to be less for DLC samples than OH-terminated SAMs.

D. Characterization of the oxidized layer on DLC surface

It is very important to notice that the oxygen concentration detected in XPS (9~14%; similar results in refs. 14 and 15) is too high to assign it to monolayer thick organic contaminants or chemisorbed oxygenated species on the DLC surface. If we calculate the *average* thickness of the oxygen-containing layer of DLC from the measured C:O atomic concentration ratio (Figure 2b) using the inelastic mean free path of photoelectrons and assuming the atomic ratio of C:O to be 1:1, the layer thickness is estimated to be ~0.7 nm. But, it is unlikely that all carbon atoms in this layer are oxidized into C-OH, C-O-C, C=O, and O-C=O. If the fraction of the oxidized carbon species is ~25% and the rest is C-C/C-H species, the thickness of the oxygen-containing layer is estimated to ~2.1 nm [17]. This estimation is in good agreement with the depth profiling result showing that the oxygen XPS intensity decreases below the detection limit after removal of the top 2~3 nm layer with argon ion sputtering [18].

The formation of thick oxidized layers must be related to the presence of dangling bonds in the DLC structure inevitably produced during the deposition process or the frictional sliding. The incorporation of hydrogen reduces the dangling bonds, but some may remain and react with oxygen or water upon exposure to ambient air. In the case of metallic surfaces, it is well known that a few nanometers thick oxide layer can be readily formed even at very low oxygen partial pressures and room temperature if its formation can reduce the surface energy of the solid [19]. Good examples are the native oxide formation on silicon and aluminum. Similarly, it appears that once the sample is exposed to air, the oxidation of the DLC surface containing dangling bonds or other reactive carbon species seems to occur spontaneously to an equilibrium level determined by the given oxygen and water partial pressures. This could interfere with our wish to find the chemical composition of the DLC surface in controlled gas environments from ex-situ analysis (Figures 2b and 2c). This also suggests that the run-in behavior of DLC could be due to frictional removal of the 2~3 nm thick oxidized layer of the DLC coating.

Chemical derivatization reactions were employed to assist XPS identification of functional groups in the oxidized surface layer of DLC exposed to air [17]. For distinction of hydroxyl (C-OH) or ether (C-O-C) groups, trifluoroacetic anhydride (TFAA) was utilized to selectively differentiate the hydroxyl group. The main challenge in applying this chemistry to the DLC film is that the oxygenated species is not all exposed at the film surface and some are imbedded in the sub-surface. As a simple approximation, it was assumed that the trifluoroethyl hydrazine (TFH) reaction with carbonyl groups can be used as an internal standard to estimate the overall reaction yield for the TFAA reaction with hydroxyl groups and the 286.5 eV peak of C1s XPS was deconvoluted into hydroxyl and ether components. The high reaction yield and selectivity of TFAA and TFH were confirmed with SAMs and polymer reference samples. It was found that the oxidation products are mostly ether, carbonyl, carboxyl species and a smaller amount of hydroxyl species. The data are summarized in Table 1.

Table 1. Concentration of functional groups in the oxidized layer of air-exposed DLC samples determined by chemical derivatization assisted XPS analysis [17].

DLC	C-C/C-H	C-OH	C-O-C	C=O	O-C=O
Ethanol-cleaned	85.6±1.0	1.2±0.3	4.1±0.6	5.0±0.5	4.1±0.2
Plasma-cleaned	85.5±1.0	0.9±0.4	5.1±0.6	4.6±0.9	4.0±0.5

E. Enhancing chemical imaging contrast with selective derivatization

We have tested if the selective chemical derivatization reaction can be utilized to enhance chemical imaging capability of XPS and Auger electron spectroscopy (AES). However, the x-ray and electron-beam induced damages of the organic functional groups were too severe to allow high resolution chemical imaging of oxygenated functional groups. This is illustrated in Figure 3 which shows the decrease of differentiated Cl and F peaks upon consecutive scans in AES analysis [20]. The disappearance of F and Cl is caused by the electron-stimulated dissociation and desorption [21]. To avoid the x-ray and electron-beam induced damage problems, one can use ToF-SIMS. To demonstrate this, a chemically patterned SAM sample ($25\mu\text{m} \times 25\mu\text{m}$ square regions with COOH groups separated by $25\mu\text{m}$ wide regions with OH groups) was prepared and derivatized with Ba(OH)₂ and TFAA. Ba(OH)₂ adsorbs only on the COOH functional group and TFAA reacts selectively with the OH group. Figure 4c shows the selective derivatization of these two chemically distinct regions and successful imaging with ToF-SIMS [22].

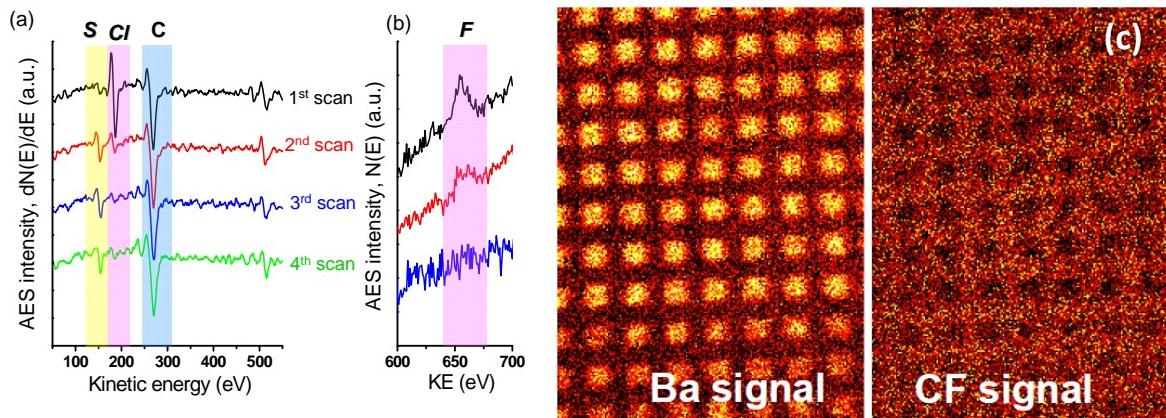


Figure 3. Changes in AES spectra of OH-SAMs on gold chemically derivatized with (a) Cl and (b) F upon repeated scans showing the electron-stimulated dissociation and desorption of the chemical tags [20]. (c) ToF-SIMS images of Ba and CF signals from chemically derivatized COOH/OH patterned SAM sample [22].

We explored an alternative derivatization agent that is suitable to enhance the chemical imaging of XPS and AES and found that inorganic nanoparticles would work better than the organic derivatization reactions. Figure 4 shows a preliminary result showing the feasibility of

using zinc hydroxide particles to selectively decorate the COOH functional groups co-present with the OH group [20]. Apparently, ZnO nanoparticles were adsorbed only onto the COOH regions after immersing the sample in unfiltered $\text{Zn}(\text{OH})_2/\text{ZnCO}_3$ solution for 30 minutes.

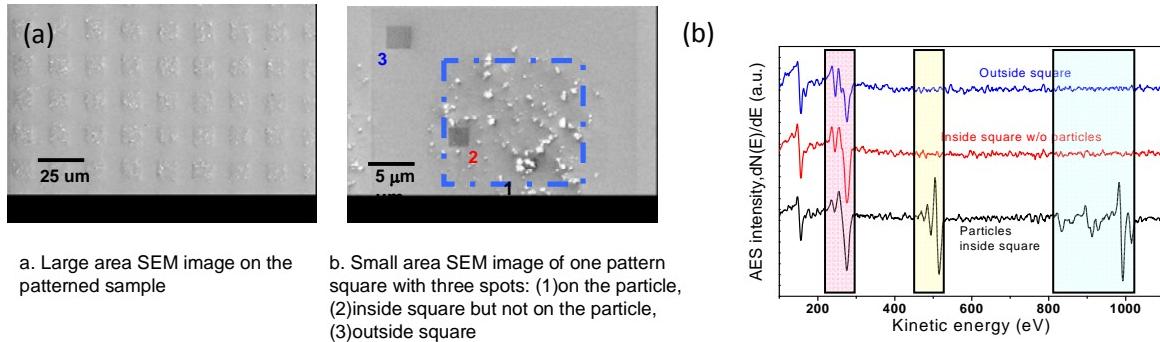


Figure 4. (a) Scanning electron micrograph of the COOH-SAM square regions separated by the OH-SAM region after immersion into a solution containing $\text{Zn}(\text{OH})_2/\text{ZnCO}_3$ particulates. (b) Comparison of AES spectra of the adsorbed particles adsorbed inside the COOH-SAM region and the OH-SAM region [20].

F. Adsorption isotherm of water on DLC

Water vapor has the most detrimental effect on the friction and wear behavior of highly-hydrogenated DLC coatings (Figure 2a). In order to understand the role of the adsorbed water layer, it is extremely important to know the thickness and structure of the water layer on the DLC surface. The adsorption isotherm of water molecules on DLC under ambient pressure conditions were determined using ATR-IR spectroscopy and ellipsometry. We have measured the water adsorption isotherm on DLC using a single-wavelength ellipsometer and found that the water layer thickness is estimated to be about 1 nm at relative humidity between 15% and 80% [23]. More accurate determination of the layer thickness and structure can be obtained from ATR-IR spectroscopy. A thin NFC-6 coating (~70 nm thick) was deposited on a Si ATR crystal. Figure 5 shows the water adsorption and desorption isotherm data for the NFC-6 coating [24]. Once the refractive index of the NFC-6 film in the infrared region is measured with spectroscopic ellipsometry (which is arranged to be done in the near future), the ATR-IR intensity can be converted to the thickness of the adsorbed water. The ATR-IR spectra of the adsorbed water on DLC reveal that there are three types of hydrogen bonding interactions in the water layer – weakly hydrogen bonded (peak at $\sim 3600\text{cm}^{-1}$), liquid-like structure (peak at $\sim 3400\text{cm}^{-1}$), and solid-like structure (peak at $\sim 3230\text{cm}^{-1}$). As the relative humidity increases the liquid-like structure becomes dominant. When the relative humidity is decreased, the data clearly show that not all water molecules are desorbed and the solid-like structure become dominant in the water layer remaining on the DLC surface upon drying. Not only the thickness but also the structure of the adsorbed water layer have significant impacts on the capillary force of nano-asperity contacts [25] that may exist at tribological interfaces of DLC.

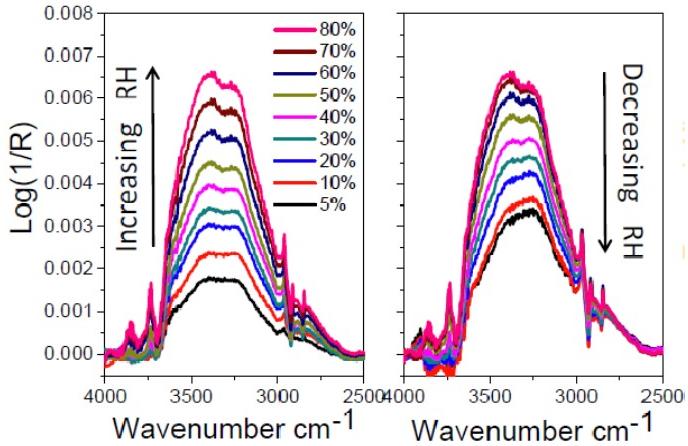


Figure 5. ATR-IR spectra of adsorbed water on NFC-6 while changing RH from zero to 80% and back [24].

G. Theoretical understanding of nano-asperity capillary force

A theoretical model was developed to accurately calculate the capillary force at a nanoscale asperity contact due to adsorbed molecular layers [26]. As shown in Figure 5, a molecular adsorbate layer is readily formed on solid surface in ambient conditions unless the surface energy of the solid is low enough and unfavorable for vapor adsorption. Then, the capillary meniscus formed around the solid asperity contact should be in equilibrium with the adsorbate layer, not with the bare solid surface. However, the conventional models assume that the solid surface is free of adsorbate and consider the vapor-liquid equilibrium (via Young-Laplace and Kelvin equations) and the liquid-solid equilibrium (via liquid contact angle) [27]. Although various hypotheses on the nanoscale capillary phenomena have previously been proposed, the models assuming adsorbate-free solid surfaces do not explicitly explain the experimentally observed partial pressure dependence of the capillary force. Especially, the partial pressure dependence of the capillary force is not explained clearly in calculations with the conventional models. Thus, the friction coefficient increase with the relative humidity has often been ascribed to the capillary effect without clear physical explanations or justifications.

We have developed a theoretical model incorporating the vapor adsorption isotherm into the solution of the Young-Laplace equation. Two contact geometries (sphere-on-flat and cone-on-flat) as well as the meniscus contact angle are considered. The model is based on two assumptions: (1) the solid surface is smooth and (2) the meniscus meets with the adsorbate layer on the solid surface which is in equilibrium with the vapor phase, instead of the bare solid surface. Figure 6 schematically explains how the adsorption isotherm is incorporated into the theoretical model. In order to mathematically compare the partially wetting interface with the completely wetting interface, the adsorbate thickness is assumed to a function of $\cos(\theta)$ where θ is the liquid-solid contact angle. The model constructed with a proper vapor adsorption isotherm explains well the vapor partial pressure dependence of the capillary force observed experimentally for completely wetting surfaces [28]. The large relative partial pressure dependence mainly comes from the change in the meniscus size due to the presence of the

adsorbate layer (Figure 6b). In contrast, the model ignoring the adsorption isotherm predicts insignificant partial pressure dependence, which is inconsistent with the experimental data. These theoretical results imply that the continuous increase of the friction coefficient of DLC films with increase of the relative humidity cannot be explained with the capillary effect only. If the capillary effect was the dominant factor in the environmental effects of DLC friction, then the friction coefficient should decrease as the relative humidity increases and approaches to the saturation point, which is not the case observed experimentally [29-32].

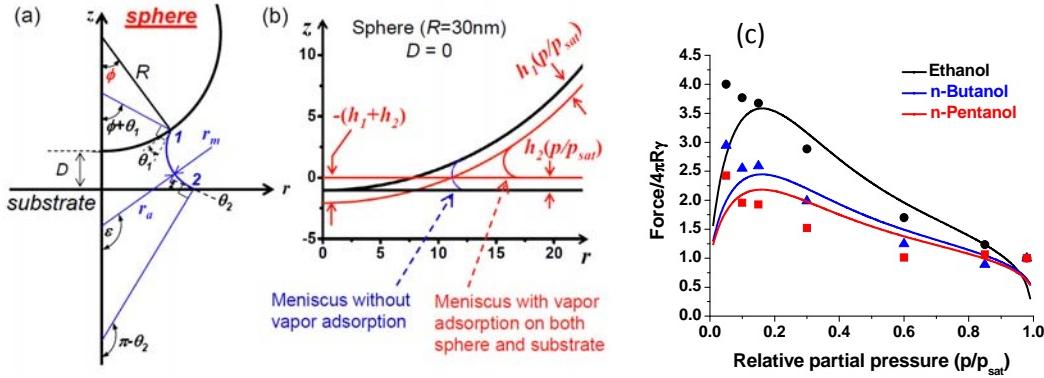


Figure 6. (a) Geometrical presentation of a liquid bridge between a sphere and a flat substrate. (b) Meniscus profiles created with our theoretical model for a sphere with a radius of 30 nm without (blue line) and with (red line) considering the equilibrium thickness of the adsorbed ethanol layer on the sphere, $h_1(p/p_{sat} = 0.7)$, and the thickness on the flat substrate, $h_2(p/p_{sat} = 0.7)$. The meniscus contact angle is set to $\theta_1 = \theta_2 = 0^\circ$. (c) Comparison between the theoretical calculation with the adsorption isotherm and the experimentally observed trend. The experimental data are obtained from Ref. [28].

H. Vapor phase lubrication of DLC sliding against stainless steel with alcohol

The effects of n-pentanol vapor on friction and wear of hydrogenated diamond-like carbon (DLC) films during sliding against a 440C stainless steel (SS) ball were investigated with a reciprocating pin-on-disc tribometer. When the friction is measured with a counterface made of different material (such as oxide, metals, nitride) sliding against the DLC surface, the induction or run-in period is inevitably observed before the sliding interface enters the steady-state low-friction and low-wear regime. When the ball surface is analyzed after friction test, there is almost always a carbon transfer film in and around the contact area of the counter-surface [33]. Once the carbon transfer film is formed on the counter-surface, then the friction coefficient and the wear rate are very low. So, it is generally accepted that the transfer film formation is inevitable and necessary to attain low friction and low wear for foreign materials rubbing against DLC.

It was discovered that in an Ar environment containing n-pentanol vapor, the wear and transfer film formation of the DLC surface is remarkably suppressed although the friction coefficient is not ultra-low (<0.01) but in the vicinity of ~0.15 (Figures 7 and 8) [23]. In the n-pentanol vapor environment, the initial change in friction coefficient is insignificant. These results are contrast to the friction and wear behaviors of the SS440C/DLC interface in the dry and humid argon environments.

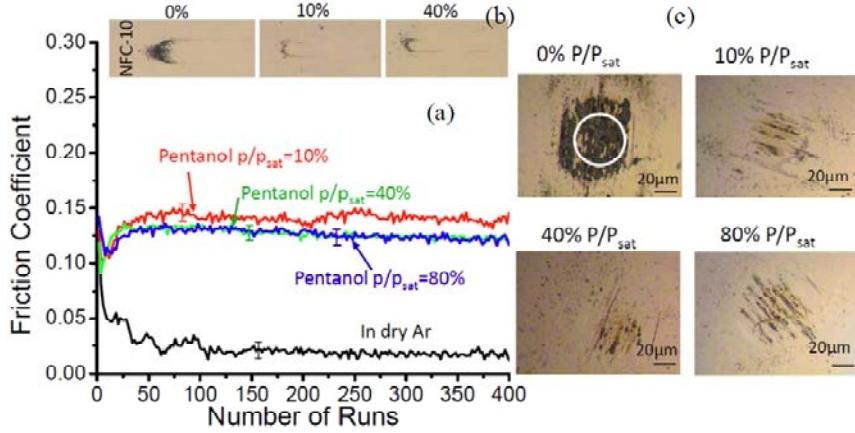


Figure 7. (a) Friction coefficients for a SS440C ball sliding on a mildly-hydrogenated carbon in dry and varying pressures of n-pentanol in Ar. Optical microscopy images of (b) the substrate and (c) the ball after 400 cycles of bi-directional sliding [23].

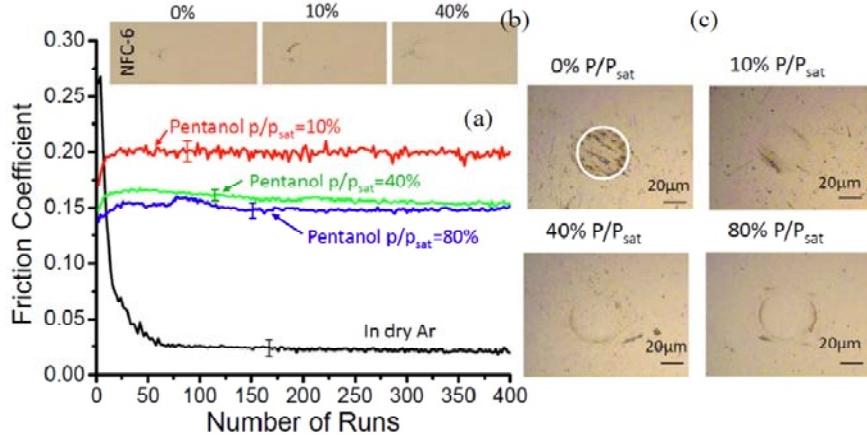


Figure 8. (a) Friction coefficients for a SS440C ball sliding on a highly-hydrogenated carbon in dry and varying pressures of n-pentanol in Ar. Optical microscopy images of (b) the substrate and (c) the ball after 400 cycles of bi-directional sliding [23].

The good alcohol VPL efficiency for wear prevention and negligible run-in period imply that the alcohol molecules readily adsorb and modify the DLC surface. An x-ray photoelectron spectroscopy analysis finds that the DLC surface is oxidized before the friction test begins. Once the oxidized carbon surface is fully covered with the adsorbed alcohol layer (or chemisorbed alkoxide molecules at some surface sites), then the shear stress of the interface mediated with alcohol molecules seem to be low enough to prevent the rupture of the underlying carbon surface. As long as the vapor pressure of alcohol is kept above a certain level, the substrate surface is always fully covered with the adsorbate molecules (Figure 4). It should be noted that the friction coefficient of most self-assembled monolayers (SAMs) of organic molecules on solid surfaces exhibit a friction coefficient of 0.1~0.2 [34-36], which is comparable to the friction coefficient observed for the n-pentanol vapor lubricated SS440C/DLC interface. The alcohol VPL of the SiO₂ surface also shows a friction coefficient of ~0.15 [37, 38]. These comparisons of the friction coefficient values imply that the SS440C/DLC interface is well lubricated with the adsorbed alcohol molecules so that the DLC wear is suppressed although the friction coefficient

is not ultra-low. Further study on fundamental lubrication mechanism of alcohol adsorption of DLC surfaces is required to fully enable the alcohol vapor phase lubrication of DLC coatings.

I. Wear prevention of DLC in humid air using alcohol vapor phase lubrication

Finally, it is of great interest to test if the presence of n-pentanol vapor can protect the DLC surface even in humid air where DLC is known to perform poorly. Preliminary test result is shown in Figure 9 [13], and the result is very promising. When 40% p/p_{sat} n-pentanol ($p_{\text{pentanol}}=0.9$ Torr) is introduced into 40% RH ($p_{\text{water}}=9.6$ Torr) air, the run-in behavior as well as the surface wear of DLC are almost completely suppressed. It is especially important to note that, regardless of the hydrogen content in the DLC film, no wear is observed in the n-propanol-containing humid air even though the steady-state friction coefficient is not ultra-low but it is as high as ~ 0.13 . The air-oxidized surface layer of DLC appears to be well protected by the adsorbed n-pentanol molecule on the surface. These findings can open a new ways of controlling the friction and wear behaviors of DLC coatings especially in O₂- and H₂O-containing environments which has conventionally been known to be chemically harsh or non-ideal for the operation of DLC coatings. Further study is needed to understand the wear prevention mechanism and achieve ultra-low friction via vapor phase lubrication in humid air conditions, which will lead the enabling energy-conserving and long-lasting coating technologies for mechanical systems subject to constant friction and wear during their normal operations.

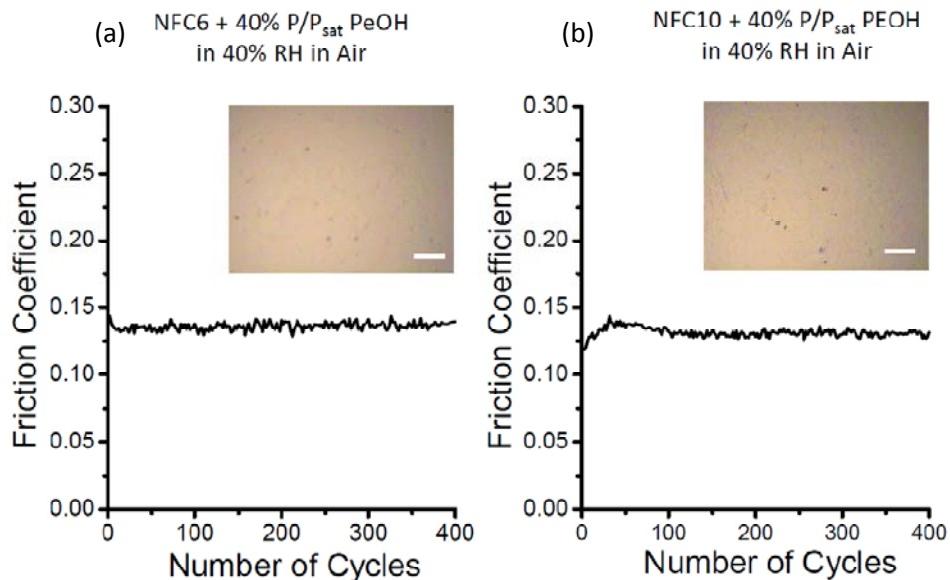


Figure 9. Friction coefficients for self-mated (a) highly-hydrogenated DLC (NFC-6) and (b) poorly-hydrogenated DLC (NFC-10) measured in humid air (40% RH; $p_{\text{water}} = 9.6$ Torr) containing 40% p/p_{sat} n-pentanol ($p_{\text{pentanol}}=0.9$ Torr). The insets show optical microscope images of the ball surfaces after the friction test [13].

References

1. C. Donnet, A. Erdemir, Tribology of Diamond-Like Carbon Film. Springer, New York, 2008.
2. Erdemir A. Eryilmaz O.L. Fenske G., Synthesis of diamondlike carbon films with superlow friction and wear properties. *Journal of Vacuum Science & Technology A* 2000; 18(4):1987-1992.
3. Donnet C. Erdemir A., Solid lubricant coatings: recent developments and future trends. *Tribology Letters* 2004; 17(3):389-397.
4. S.H. Kim, Environmental Effects in Tribology. In Micro- and Nanoscale Phenomena in Tribology, Chung, Y.W., Ed. Taylor & Francis Group (2011), Chapter 6.
5. C. Donnet, J. Fontaine, A. Grill, T. Le Mogne, "The Role of Hydrogen on the Friction Mechanism of Diamond-like Carbon Films" *Tribol. Lett.* 9, 137-142 (2000)
6. O. L. Eryilmaz, A. Erdemir, M. J. Marino, and S. H. Kim "The effect of hydrogen and deuterium on friction behavior of diamondlike carbon films: an imaging ToF-SIMS study" (manuscript in preparation).
7. T. Numata, H. Nanao, S. Mori, S. Miyake, Chemical analysis of wear tracks on magnetic disks by TOF-SIMS, *Tribology International* 36 (2003) 305-309.
8. O.L. Eryilmaz, A. Erdemir, On the hydrogen lubrication mechanism(s) of DLC films: An imaging TOF-SIMS study, *Surface & Coatings Technology* 203 (2008) 750-755.
9. Scharf T.W. Singer I.L. Role of third bodies in friction behavior of diamond-like nanocomposite coatings studied by in situ tribometry. *Tribology Transactions* 2002; 45(3):363-371.
10. Donnet C. Belin M. Auge J. C. Martin J. M. Grill A. Patel V., Tribocchemistry of Diamond-Like Carbon Coatings in Various Environments. *Surface & Coatings Technology* 1994; 68:626-631.
11. Donnet C. Le Mogne T. Ponsonnet L. Belin M. Grill A. Patel V. Jahnes C., The respective role of oxygen and water vapor on the tribology of hydrogenated diamond-like carbon coatings. *Tribology Letters* 2004; 4(3):259-265.
12. A. P. Merkle, A. Erdemir, O. L. Eryilmaz, J. A. Johnson, L. D. Marks, "In-situ TEM studies of tribo-induced bonding modifications in near-frictionless carbon films", *Carbon*, 48(2010)587-591.
13. M. J. Marino, E. Hsiao, Y. Chen, O. L. Eryilmaz, A. Erdemir, and S. H. Kim "Understanding Run-In Behavior of Diamond-Like Carbon (DLC) Friction and Preventing DLC Wear in Humid Air" (manuscript in preparation).
14. O.L. Eryilmaz, A. Erdemir, Surface analytical investigation of nearly-frictionless carbon films after tests in dry and humid nitrogen, *Surface & Coatings Technology* 201 (2007) 7401-7407.
15. O.L. Eryilmaz, A. Erdemir, TOF-SIMS and XPS characterization of diamond-like carbon films after tests in inert and oxidizing environments, *Wear* 265 (2008) 244-254.
16. J.A. Johnson, J.B. Woodford, X.D. Chen, J. Andersson, A. Erdemir, G.R. Fenske, Insights into "near-frictionless carbon films", *Journal of Applied Physics* 95 (2004) 7765-7771.
17. M. Yang, M. J. Marino, V. J. Bojan, O. L. Eryilmaz, A. Erdemir, and S. H. Kim, "Quantification of oxygenated species on a diamond-like carbon (DLC) surface" *Appl. Surf. Sci.* (in revision).

18. N.J. Mehta, S. Roy, J.A. Johnson, J.B. Woodford, A. Zinovev, Z. Islam, A. Erdemir, S. Sinha, G.R. Fenske, B. Prorok, X-Ray studies of near-frictionless carbon films, *Materials Research Society Symposium Proceedings* 843 (2005) T2.7.1-T2.7.6.
19. C.T. Campbell, Transition metal oxides: Extra thermodynamic stability as thin films, *Physical Review Letters* 96 (2006) 066106.
20. M. Yang "Development of chemical imaging methods for organic functional groups on model surfaces" MS Thesis, Pennsylvania State University (2009).
21. Seshadri, K.; Froyd, K.; Parikh, A. N.; Allara, D. L.; Lercel, M. J.; Craighead, H. G. *Journal of Physical Chemistry* **1996**, *100*, 15900-15909.
22. Matthew J. Marino "Environmental effects on the friction, wear, and tribocorrosion of diamond-like carbon films" MS Thesis, Pennsylvania State University (2010).
23. M. J. Marino, E. Hsiao, L. C. Bradley, O. L. Eryilmaz, A. Erdemir, and S. H. Kim, "Is ultra-low friction needed to prevent wear of diamond-like carbon (DLC)? – An alcohol vapor lubrication study for stainless steel / DLC interface" *Tribol. Lett.* (in press).
24. A. J. Barthel, A. L. Barnette, O. L. Eryilmaz, A. Erdemir, and S. H. Kim (unpublished result).
25. D. B. Asay and S. H. Kim, "Effects of Adsorbed Water Layer Structure on Adhesion Force of Silicon Oxide Nanoasperity Contact in Humid Ambient" *J. Chem. Phys.* **2006**, *124*, 174712.
26. E. Hsiao, M. J. Marino, S. H. Kim, "Effects of gas adsorption isotherm and liquid contact angle on capillary force for sphere-on-flat and cone-on-flat geometries" *Journal of Colloid and Interface Science* 352 (2010) 549–557.
27. H.J. Butt, M. Kappl, "Normal capillary forces" *Adv Colloid Interface Sci.* 146 (2009) 48.
28. D.B. Asay, S.H. Kim, "Molar Volume and Adsorption Isotherm Dependence of Capillary Forces in Nanoasperity Contacts" *Langmuir*. 23 (2007) 12174.
29. C. Donnet, M. Belin, J.C. Auge, J.M. Martin, A. Grill, V. Patel, TRIBOCHEMISTRY OF DIAMOND-LIKE CARBON COATINGS IN VARIOUS ENVIRONMENTS, *Surface & Coatings Technology* 68 (1994) 626-631.
30. C. Donnet, T. Mogne, L. Ponsen, M. Belin, A. Grill, V. Patel, C. Jahnes, The respective role of oxygen and water vapor on the tribology of hydrogenated diamond-like carbon coatings, *Tribology Letters* 4 (1998) 259-265.
31. H.I. Kim, J.R. Lince, O.L. Eryilmaz, A. Erdemir, Environmental effects on the friction of hydrogenated DLC films, *Tribology Letters* 21 (2006) 53-58.
32. O.L. Eryilmaz, A. Erdemir, Surface analytical investigation of nearly-frictionless carbon films after tests in dry and humid nitrogen, *Surface & Coatings Technology* 201 (2007) 7401-7407.
33. Erdemir, A., Bindal, C., Fenske, G. R., Zuiker, C., Wilbur, P.: Characterization of transfer layers forming on surfaces sliding against diamond-like carbon. *Surf Coat Technol* 86-7, 692-697 (1996).
34. Sambasivan, S., Hsieh, S., Fischer, D. A., Hsu, S. M.: Effect of self-assembled monolayer film order on nanofriction. *J Vac Sci Technol*, A 24, 1484-1488 (2006)
35. Khatri, O. P., Biswas, S. K.: Friction of octadecyltrichlorosilane monolayer self-assembled on silicon wafer in 0% relative humidity. *J Phys Chem B* 111, 2696-2701 (2007)

36. Choi, J., Kawaguchi, M., Kato, T.: Possibility of organic monolayer films as lubricants for disk drives: Comparative study of PFPE and organosilane. *J Tribol - Trans ASME* 125, 850-853 (2003)
37. Asay, D. B., Dugger, M. T., Ohlhausen, J. A., Kim, S. H.: Macro- to nanoscale wear prevention via molecular adsorption. *Langmuir* 24, 155-159 (2008)
38. Barnette, A. L., Asay, D. B., Kim, D., Guyer, B. D., Lim, H., Janik, M. J., Kim, S. H.: Experimental and Density Functional Theory Study of the Tribocatalytic Wear Behavior of SiO₂ in Humid and Alcohol Vapor Environments. *Langmuir* 25, 13052-13061 (2009)

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Publications/Accepted or In Print:

1. "Understanding Run-In Behavior of Diamond-Like Carbon (DLC) Friction and Preventing DLC Wear in Humid Air" M. J. Marino, E. Hsiao, Y. Chen, O. L. Eryilmaz, A. Erdemir, and S. H. Kim (manuscript in preparation)
2. "Quantification of oxygenated species on a diamond-like carbon (DLC) surface" M. Yang, M. J. Marino, V. J. Bojan, O. L. Eryilmaz, A. Erdemir, and S. H. Kim, *Appl. Surf. Sci.* (in revision).
3. "Is ultra-low friction needed to prevent wear of diamond-like carbon (DLC)? – An alcohol vapor lubrication study for stainless steel / DLC interface" M. J. Marino, E. Hsiao, L. C. Bradley, O. L. Eryilmaz, A. Erdemir, and S. H. Kim, *Tribol. Lett.* (in press).
4. S.H. Kim, Environmental Effects in Tribology. In *Micro- and Nanoscale Phenomena in Tribology*, Chung, Y.W., Ed. Taylor & Francis Group (2011), Chapter 6.
5. "Effects of gas adsorption isotherm and liquid contact angle on capillary force for sphere-on-flat and cone-on-flat geometries" E. Hsiao, M. J. Marino, S. H. Kim, *Journal of Colloid and Interface Science* 352 (2010) 549–557.
6. "MEMS lubrication with alcohol vapour" S. H. Kim, M. T. Dugger, A. Erdemir, A. L. Barnette, E. Hsiao, M. J. Marino, and O. Eryilmaz, *Tribology*, 2010, 4, 109-114.
7. "The effect of hydrogen and deuterium on friction behavior of diamondlike carbon films: an imaging ToF-SIMS study" O. L. Eryilmaz, A. Erdemir, M. J. Marino, and S. H. Kim (manuscript in preparation).
8. "In-situ TEM studies of tribo-induced bonding modifications in near-frictionless carbon films", A. P. Merkle, A. Erdemir, O. L. Eryilmaz, J. A. Johnson, L. D. Marks, *Carbon*, 48(2010)587-591.
9. "Tribology and tribochemistry on non-hydrogenated amorphous carbon coatings under boundary lubrication conditions", Matta, C.; Eryilmaz, O. L.; Martin, J.-M.; Erdemir, A., Proceedings of 17th International Colloquium Tribology Solving Friction and Wear Problems; Stuttgart/Ostfildern, Germany; Jan. 19, 2010 - Jan. 21, 2010.
10. "The Role of Hydrogen and Deuterium in Tribological Performance of Diamondlike Carbon Films: An Imaging TOF-SIMS Study", A. Erdemir and O. L. Eryilmaz, Proceedings of the 2nd International Conference on Science of Friction, Nagoya, Japan, September 12-17, 2010.

Interactions/Transitions**(a) Participation/presentations at meetings, conferences, seminars, etc. during report period:**

1. "Understanding Environmental Effects of DLC and Preventing DLC Wear via Alcohol Vapor Lubrication" Matthew J. Marino, Osman L. Eryilmaz, Ali Erdemir, Seong H. Kim, 2011 STLE Annual Meeting, May 15-19, 2011, Atlanta, Georgia.

2. "Understanding and solving tribology and lubrication issues of MEMS" Invited talk presented at 2010 MRS Fall Symposium, Nov. 29 – Dec. 2, 2010, Boston, MA.
3. "Understanding Vapor Phase Lubrication Mechanism of Alcohol for MEMS and Other Materials" Seong H. Kim, AVS 57th International Symposium, October 17 - 22, 2010, Albuquerque, NM
4. "Nanotribology and lubrication of microelectromechanical systems" Seong H. Kim, Invited talk presented at 3rd Int'l Conference on Multi-Functional Materials and Structures (MFMS), Korea, Sept 14-18, 2010
5. "Effects of equilibrium vapor adsorption on capillary force" S. H. Kim, M. P. de Boer, 240th ACS meeting, August 22 – 26, 2010, Boston, MA.
6. "Vapor Phase Lubrication - Nanotribology Fundamentals and Applications" Seong H. Kim, Invited talk presented at Nano-tribology and related Materials Issues in MEMS, National University of Singapore, May 13-14, 2010.
7. "Chemical Issues at Tribological Interfaces" NSF Summer Institute on Nanomechanics, Nanomaterials, and Micro/Nanomanufacturing Micro and Nano Scale Phenomena in Tribology, April 24 – 25, 2010, San Diego, CA.
8. "From fundamentals of adsorption isotherm and molecular orientation to successful lubrication operations" S. H. Kim, Invited talk presented at Micro-Tribology 2009, September 21-22, 2009, Milowka, Poland.
9. "An imaging of TOF-SIMS study of the tribochemical interactions in diamondlike carbon films", Erdemir, A.; Eryilmaz, O. L., AVS 56th International Symposium and Exhibition; San Jose, CA; Nov. 8, 2009 - Nov. 13, 2009.
10. "Advances in superhard and low-friction coatings for extreme tribological applications", Erdemir, A.; Eryilmaz, O. L.; Urgen, M.; Kazmanli, K., Invited talk, ASME/STLE International Joint Tribology Conference (IJTC 2009); Memphis, TN; Oct. 19, 2009 - Oct. 21, 2009.
11. "Tribology and tribochemistry on non hydrogentaed amorphous carbon coatings under boundary lubrication conditions", Matta, C.; Eryilmaz, O. L.; Martin, J.-M.; Erdemir, A., 17th International Colloquium Tribology Solving Friction and Wear Problems; Stuttgart/Ostfildern, Germany; Jan. 19, 2010 - Jan. 21, 2010.
12. "The Role of Hydrogen and Deuterium in Tribological Performance of Diamondlike Carbon Films: An Imaging TOF-SIMS Study", A. Erdemir and O. L. Eryilmaz, Invited Plenary Talk, presented at the 2nd International Conference on Science of Friction, Nagoya, Japan, September 12-17, 2010.
13. "Diamondlike Carbon Films and Their Tribology: Recent Advances and Applications", Invited Talk Presented to ExxonMobile Research and Engineering Company, Annandale, NJ, February 9, 2010.
14. "In situ TEM Tribological Investigation of Deformation Mechanisms in Diamond-like Carbon films" authorship of A. Tatsiwa M'ndange-Pfupfu, O. Eryilmaz, A. Erdemir and L. D. Marks, presented at the 17th International Microscopy Congress - IMC17, September 19-24, 2010, Rio de Janeiro, Brazil.
15. "Friction studies of highly-hydrogenated and non-hydrogenated amorphous carbon in inert and hydrogen atmospheres at elevated temperatures", Erck, R. Eryilmaz, O. Demas, N. Erdemir, A. Presented at the Society of Tribologists and Lubrication Engineers (STLE) 65th Annual Meeting & Exhibition, Las Vegas, NV; May 16-20, 2010.

(b) Consultative and advisory functions during report period:

New Discoveries, Inventions, or Patent Disclosures:

Honors/Awards: (during the grant period)

1. A. Erdemir was recognized as a Argonne Distinguished Fellow by Argonne National Laboratory.
2. S. H. Kim was elected for Executive Board of AVS Nanoscale Science and Technology Division.
3. S. H. Kim was a Guest Editor of *Langmuir* Special Issue “Molecular Surface Chemistry and Its Applications”
4. S. H. Kim was a Guest Editor of *Journal of Adhesion Science Technology* Special Issue “Adhesion Aspects in MEMS and NEMS”
5. S. H. Kim was a Section Editor for Gas Vapor Phase Lubrication of *Springer Encyclopedia of Tribology*
6. A. Erdemir was elected to become the Chair of AVS-Advanced Surface Engineering Division.
7. A. Erdemir was the Program Chair of International Conference on Metallurgical Coatings and Thin Films, San Diego, Ca.